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Evaluation of trickle-bed air biofilter performance for MEK removal

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Abstract

A lab-scale trickle-bed air biofilter (TBAB) was operated to evaluate the removal of methyl ethyl ketone (MEK) from waste gas. Three biomass control strategies were investigated, namely, backwashing and two non-use periods (starvation and stagnant). Five volumetric loading rates from 0.70 to 7.04 kg COD/m^3 day were employed. Backwashing once a week removed the excess biomass and obtained long-term, stable performance over 99% removal efficiency for loading rates less than 5.63 kg COD/m^3 day. The two non-use periods could also sustain 99% removal efficiency and could be employed as another means of biomass control for loading rates up to 3.52 kg COD/m^3 day. The non-use periods did not delay the recovery when the loading rate did not exceed 3.52 kg COD/m^3 day. The pseudo-first-order removal rate constant decreased with increase in volumetric loading rate. The effect of non-use periods on removal rate showed apparent transition from positive to negative with the increase in loading rate.

Keywords: MEK; TBAB; Backwashing; Non-use periods; Removal rate

1. Introduction

In response to strict regulatory demands for control of volatile organic compounds (VOCs) emissions, biofiltration systems have recently emerged as an efficient and cost-effective technology. Biofilter performance in control of VOCs is strongly affected by the type of packing materials (media) used for microbial attachment. Biofilter media are mainly of two types: natural organic media and inert synthetic media. The typical synthetic media biofilter is usually referred to as a trickle-bed air biofilter (TBAB). TBABs facilitate more consistent operation than do natural media biofilters via better control of overall pressure drop, nutrient concentration, and pH. The main disadvantage of TBABs is clogging due to excessive biomass formation and retention. Procedures for limiting excess biomass accumulation without adversely affecting the microbial effectiveness of a biofilter were investigated in previous studies [1,2].

Methyl ethyl ketone (MEK) is a commonly used solvent for lacquers, adhesives, and cleaning materials prior to electroplating. MEK can persist in the body for 12–24 h [3]. Breathing MEK can cause severe irritation of the upper respiratory tract [4]. Although MEK is not neurotoxic, it is known to potentiate the neurotoxicity caused by *n*-hexane after chronic coexposure [4,5].

Reports on the biofiltration of MEK are limited [6–12]. Most biofiltration studies were focused on influent concentration, retention time of the gas in the packing portion, liquid flow rate, and nutrient addition. Deshusses et al. [6,7] studied the transient mass balances and developed a diffusion reaction model by employing MIBK and MEK as the target contaminants in an equivolume mixture of compost and polystyrene spheres biofilter unit. The steady-state and transient-state behavior of biofilters was simulated by the model. The maximum elimination for MEK predicted was about 40 g/m^3 h (2.34 kg COD/m^3 day). In a later study, Deshusses et al. [8] investigated the transient-state behavior of a biofilter removing mixtures of MEK and MIBK from air under loading rates from 50 g/m^3 h (2.93 kg COD/m^3 day) to 90 g/m^3 h (5.28 kg COD/m^3 day) with removal efficiency

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90%. Deshusses and Johnson [9] used a mixture of mushroom compost and wood chips media and obtained a MEK elimination capacity of 30–35 g/m^3 h (1.76–2.05 kg COD/m^3 day). Chou and Huang [10] compared two biofilters performance to remove MEK packed with wood and plastic packings, respectively. The effects of nutrients, materials and surface area of the packings, loading rates, and recirculation rate of liquid on biofilter elimination capacity were investigated. The maximum removal capacity was 2.34 and 1.76 kg COD/m^3 day for plastic packing and wood packing, respectively. Moe and Li [11] compared the transient and long-term performance between a continuous-flow biofilter (CFB) and a sequencing batch biofilter (SBB) on removal of MEK. The packing medium in the system tested by Moe and Li [11] was polyurethane foam coated with activated carbon. Both the CFB and the SBB could maintain long-term 99% removal efficiency with a loading rate from 0.75 to 1.5 kg COD/m^3 day. Atoche and Moe [12] compared transient and long-term performance between CFB packed with polyurethane foam cubes coated with powder activated carbon and SBB packed with the polyurethane foam cubes on removal of mixture of MEK and toluene. The CFB and the SBB could both maintain long-term 99% removal for the mixture of MEK and toluene under a loading rate of 1.84 and 1.02 kg COD/m^3 day, respectively.

In practice a biofilter will be exposed to periods of non-use such as shutdown for factory retooling or equipment repair, or during weekends and holidays. Little research [13] has been reported on the impact of non-use periods on MEK removal. In order to achieve consistent high performance of the biofilter meeting the set regulations, the effect of non-use periods on the biofilter performance should be explored at different loadings.

The objectives of this research were to investigate the performance of a TBAB for MEK removal under organic loading rates up to 7.04 kg COD/m^3 day at an EBRT of 0.76 min. The investigation was conducted for three biomass control strategies, namely backwashing, and two non-use periods (starvation and stagnant). The goal was to maintain consistently high removal efficiencies for long-term operation. The evaluations were focused on the following operational parameters: (1) MEK loading, (2) recovery of biofilter performance after backwashing and non-use periods and (3) removal efficiency with biofilter depth under steady-state conditions and development of preliminary kinetic data.

2. Materials and methods

The laboratory-scale biofilter system was similar to that described by Sorial et al. [2] and Smith et al. [14]. The biofilter is constructed of seven cylindrical glass sections (Ace Glass Inc., Vineland, NJ) with an internal diameter of 76 mm and a total length of 130 cm. The sections are connected with high-pressure clamps. Each section is equipped with a sampling port that extends to the centre of the column. The reactor is packed with pelletized diatomaceous earth biological support media (Celite® 6 mm R-635 Bio-Catalyst Carrier; Celite Corp., Lompoc, CA) to a depth of about 60 cm. The packed media have a circular cross-section with a nominal diameter of 0.635 cm, 0.64 cm (mean) length, a sphericity of 0.84, and a specific surface of 11.9 cm^2/cm^3. The measured pellet internal and external void fractions were about 0.65 and 0.34, respectively, and the bulk density was about 0.62 g/cm^3 [15]. The biofilter was operated at a constant temperature of 20 °C and in a co-current gas and liquid downward flow mode.

The air supplied to the biofilter was purified by passing it through Balston FTIR purge gas generator (Paker Hannifin Corporation, Tewksbury, MA) for complete removal of water, oil, carbon dioxide, VOCs, and particulates. The air pressure was reduced to 20 psi (140 kPa) by a pressure control valve, both for safety and for isolating the biofilter from any pressure fluctuations in the upstream air supply. The air flow to the biofilter was set up at the rate of 3.6 L/min, regulated by a mass flow controller (MKS Model 247C four-channel readout mass flow controller, Andover, Mass). Liquid VOC was injected via a syringe pump (Harvard Apparatus, model NP 70-2208, Holliston, MA) into the air stream where it vaporized, and entered the biofilter through the topmost side port of the column.

The biofilter was equipped with an independent system for feeding intermittently a buffered nutrient solution through a misting nozzle (Corrigan Corporation, Northbrook, IL) at a feed rate of 1.5 L/day. The feed nutrient solution was only used in a pass-through-then-discard mode. The buffered solution contains all necessary macronutrients, micronutrients, and buffers, as described by Sorial et al. [2]. A spike solution of 2 M $NaNO_3$, and 0.22 M NaH_2PO_4 was added to the nutrient feed solution as the only nitrogen and phosphorous source to maintain an initial COD-to-nitrogen ratio of 50:1 and a nitrogen-to-phosphorous ratio of 4:1. $NaHCO_3$ was used as a pH buffer. Nitrate (NO_3-N) was used as the sole source of nutrient-nitrogen.

The biofilter was initially seeded with an aerobic microbial culture, which was obtained from the secondary clarifier of an activated sludge system at a municipal wastewater treatment plant.

The concentrations of MEK in the gas phase were measured by using a gas chromatograph (GC) (HP 5890, Series II, Hewlett-Packard, Palo Alto, CA) equipped with a flame ionization detector (FID). Effluent gas phase sample for CO_2 analysis were also taken by using gas-tight syringes through sampling ports in the biofilter. A GC (HP 5890, Series II, Hewlett-Packard, Palo Alto, CA) equipped with a thermal conductivity detector (TCD) was used for determining the CO_2 concentrations in the effluent gas phase. Liquid phase sample were analyzed for total carbon (TC), inorganic carbon (IC), and volatile suspended solid (VSS) concentration. TC and IC were determined by using a Shimadzu TOC 5050 analyzer (Shimadzu Corp., Tokyo, Japan). The VSS concentrations in the effluent and backwashing water were determined according to Standard Methods 2540 G [16].

Table 1
Operating conditions and strategies

	I	II	III	IV	V
Experimental conditions					
Inlet concentration (ppmv)	50	100	250	500	400
Loading rate (kg COD/m^3 day)	0.70	1.41	3.52	7.04	5.63
EBRT (min)	0.76	0.76	0.76	0.76	0.76
Operating periods in days					
Backwashing	1–35	80–95	136–154	197–225	269–309
Non-use period					
Starvation (2 days/week)	36–56	96–112	155–174	226–244	–
Stagnant (2 days/week)	57–79	113–135	175–196	245–268	–

Comprehensive investigations were conducted on the biofilter system for five different employed loading rates from 0.70 to 7.04 kg COD/m^3 day. For each loading rate employed, one biomass control strategy, referred to as the "backwashing" strategy, and two non-use strategies, named "starvation" strategy and "stagnant" strategy, were conducted as summarized in Table 1.

Backwashing strategy. The backwashing was conducted while the biofilter was off line by recycling 18 L of the buffered nutrient solution at a rate sufficient enough to fluidize the media for a defined time period. Finally, the recycle was shut off and another 18 L of the buffered nutrient solution was passed through the column as a rinse. The backwashing duration and frequency were initially set at 1 h duration per week for a period of three weeks for each loading rate (when the employed loading rate exceeded 1.41 kg COD/m^3 day, the backwash duration was extended to 2 h).

Starvation strategy. This experimental strategy involves the period without MEK loading, i.e., pure air with nutrient flow through the biofilter. The duration and frequency for this strategy were 2 days per week for a period of 3 weeks at MEK loadings of 0.70, 1.41, 3.52, or 7.04 kg COD/m^3 day.

Stagnant strategy. This experimental strategy reflects no flow, i.e., no nutrients, MEK loading, or air passing through the biofilter. The duration and frequency for this strategy were 2 days per week for a period of 3 weeks at MEK loadings of 0.70, 1.41, 3.52, and 7.04 kg COD/m^3 day.

3. Results and discussion

3.1. Biofilter performance

The biofilter was started up at 50 ppmv MEK inlet concentration with a corresponding loading of 0.70 kg COD/m^3 day and 0.76 min EBRT. The operating condition and strategies are summarized in Table 1. The biofilter performance with respect to MEK removal at different loading rates is presented in Fig. 1. In stage I under an employed loading rate of 0.70 kg COD/m^3 day, after about 20 days from start-up period, the biofilter maintained consistently high removal efficiency above 99%. This efficiency was maintained for all three strategies (backwashing and the two non-use strategies: starvation and stagnant). On day 80, after back-

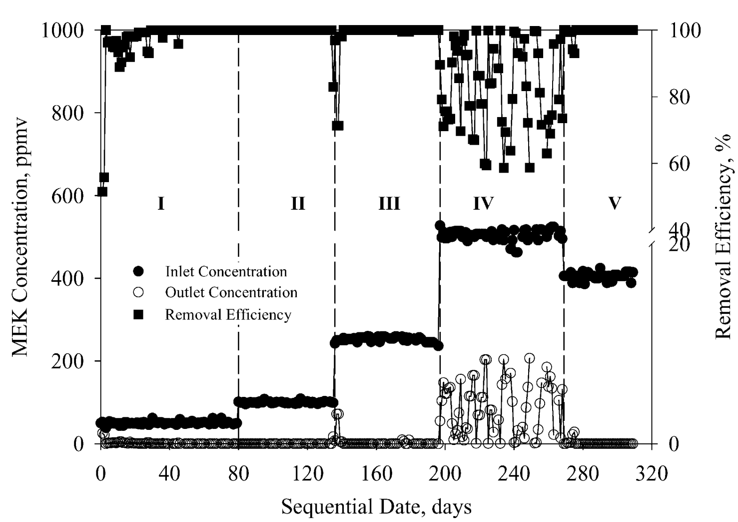

Fig. 1. Biofilter performance with respect to MEK removal at different loading rates: (I) 0.70 kg COD/m^3 day, (II) 1.41 kg COD/m^3 day, (III) 3.52 kg COD/m^3 day, (IV) 7.04 kg COD/m^3 day and (V) 5.63 kg COD/m^3 day.

washing was conducted, the loading rate was increased to 1.41 kg COD/m^3 day. No apparent acclimation period to the new higher loading rate was observed. The biofilter maintained stable, long-term removal efficiency above 99% during the duration of the three strategies. On day 136, after backwashing was conducted, the employed loading rate was increased to 3.52 kg COD/m^3 day. A period of 5 days was required to acclimate to the new loading rate. After that, the biofilter maintained consistently high removal efficiency above 99% during the duration of the three operating strategies.

On day 197, after backwashing was conducted, the employed loading rate was increased further to 7.04 kg COD/m^3 day. The biofilter could not be maintained at the 99% removal efficiency level. During the backwashing strategy, the biofilter recovered to the 99% removal efficiency level just after backwashing, then, its efficiency decreased gradually to around 60% removal just prior to the next backwashing period. During the non-use strategies, in order to improve the overall removal efficiency, backwashing was employed as the active biomass control. However, the biofilter could not maintain the 99% removal level; it decreased to 60–70% removal efficiency just prior to the next backwashing. It was observed during backwashing that the biomass accumulated in the biofilter bed was very thick and was attached on the media firmly. Therefore, backwashing once a week was thought to be not enough to remove excessive accumulated biomass under current 7.04 kg COD/m^3 day loading rate. To maintain consistent 99% removal efficiency, more frequent backwashing operation was required. It was then deduced that the employed 7.04 kg COD/m^3 day loading rate exceeded the maximum elimination capacity under current operating parameters. Therefore, lower MEK loading rate was employed in the following experimental runs. In order to determine the maximum loading rate that will provide stable 99% removal efficiency under weekly backwashing, on day 269 after backwashing, the loading rate was decreased to 5.63 kg COD/m^3 day. After 1 week acclimation, the biofilter maintained 99% removal efficiency during a period of 5 weeks under the backwashing strategy.

The MEK biofilter performance at different loading rates under the backwashing strategy and the two non-use strategies indicated the following:

1. Backwashing of the biofilter once a week removed the excess biomass and attained stable, long-term performance over 99% removal efficiency for loading rates less than 5.63 kg COD/m^3 day.
2. Non-use periods could be considered as another means of biomass control for loading rates below 3.52 kg COD/m^3 day.

The elimination capacity with respect to loading rate is presented in Fig. 2. The figure indicates that the maximum elimination capacity of MEK studied in our biofilter system is 5.82 kg COD/m^3 day with 0.55 kg COD/m^3 day standard deviation, and the critical load is 5.63 kg COD/m^3 day.

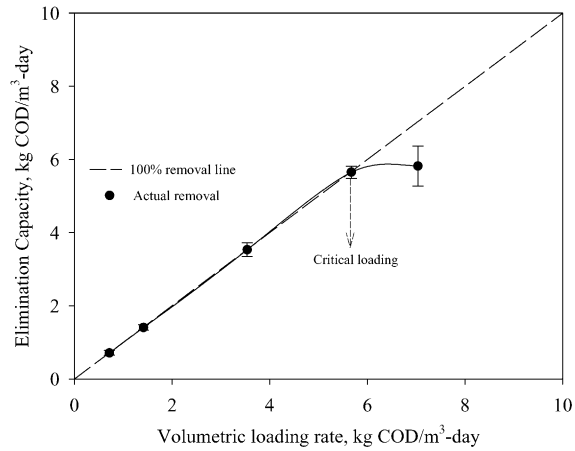

Fig. 2. Elimination capacity with respect to loading rate.

3.2. *Biofilter response after backwashing and non-use periods*

Effluent gas samples were collected at prescheduled intervals to evaluate the biofilter response subsequent to backwashing and non-use periods. Fig. 3 shows the effluent response corresponding to backwashing and two non-use periods for employed MEK loading rates of 0.70, 1.41, 3.52, and 7.04 kg COD/m^3 day and backwashing only for loading rates of 5.63 kg COD/m^3 day. Due to the high biomass accumulation for 7.04 kg COD/m^3 day loading rate, backwashing was also employed for two non-use periods. Reacclimation period was considered to have been achieved when 99% of the original biofilter performance was attained.

It can be deduced from Fig. 3 that for loading rates up to 3.52 kg COD/m^3 day, the reacclimation of the biofilter was within a short time (less than 90 min) and the non-use periods did not show negative effect on the reacclimation. These results indicate that the non-use operation could be conducted as another means for biomass control for loading rates less than 3.52 kg COD/m^3 day. For a loading rate of 7.04 kg COD/m^3 day, the biofilter reacclimated initially, and then kept decreasing. The initial reacclimation for 7.04 kg COD/m^3 day loading was thought to be due to MEK adsorption on the biomass and possibility of absorption in the water phase, not due to the real MEK biodegradation. Furthermore, the combined operation of non-use and backwashing did not show apparent improvement of the biofilter performance. For loading rates less than 5.63 kg COD/m^3 day, it is speculated that the accumulated biomass during operation in backwashing and non-use strategies was not enough to cause clogging problem. Once the employed loading exceeded the critical loading (5.63 kg COD/m^3 day), the clogging problem dominated and caused the failure of attaining consistent 99% removal.

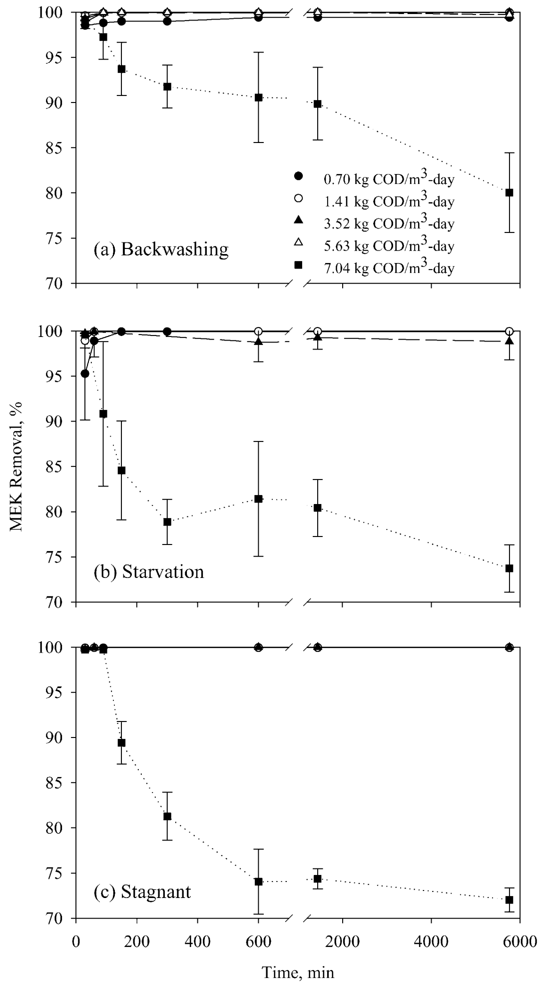

Fig. 3. Effluent response after backwashing and the two non-use period strategies for different MEK loadings.

3.3. Kinetic analysis

One day following backwashing and non-use periods, gaseous samples were taken along the media depth of the biofilter to assess removal kinetics for MEK removal. The kinetic analyses were based on pseudo-first-order removal rate as a function of biofilter depth, which was validated by the high correlation coefficients (the zero-order regression had poor correlation coefficients and high sum of squares of residuals). By plotting the natural logarithmic scale of the ratio of residual concentration to inlet concentration as a function of depth into the biofilter (expressed as the cumulative EBRT), i.e., ($\ln(C/C_0)$ versus time), the pseudo-first-order removal rate constants were obtained from the slopes of the regression lines. Fig. 4 represents plots of the MEK first-order removal rate constants under the different loading rates for the three strategies considered in this study. The result in Fig. 4 indicates that the removal rate constants decreased as the employed loading rates increased. The effect of non-use periods showed apparent transition from positive to negative. When the loading rates did not exceed

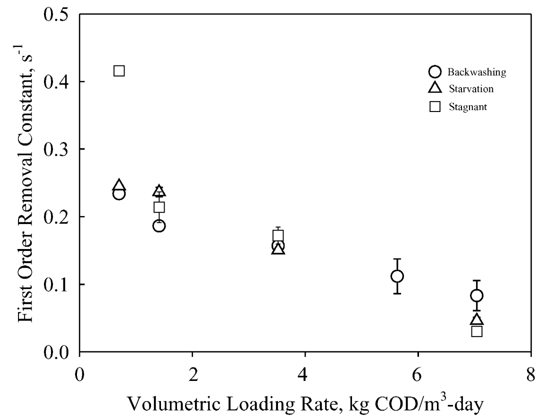

Fig. 4. First-order removal rate with respect to different MEK loading rates.

3.52 kg COD/m^3 day, the non-use operations had higher removal rates than those for backwashing operations. When the loading rate was further increased, the non-use operations had lower removal rates than those for backwashing operations. It can be deduced that non-use strategies showed high removal rates than backwashing strategy due to more available biomass during the non-use strategies when the loading rate did not exceed 3.52 kg COD/m^3 day. However, when the employed loading exceeded 3.52 kg COD/m^3 day, non-use strategies showed lower removal rates than backwashing strategy due to excessive accumulation of biomass in the biofilter bed which would eventually lead to more clogging problem.

4. Conclusion

This study evaluated the performance of a TBAB operated at different MEK volumetric loading rates ranging from 0.70 to 7.04 kg COD/m^3 day with EBRT of 0.76 min and 1.5 L/day of nutrient solution flow. Three biomass control strategies were studied, namely, backwashing and two non-use strategies (starvation and stagnant). The following points can be deduced:

1. The maximum elimination capacity was determined to be 5.82 kg COD/m^3 day and the critical loading 5.63 kg COD/m^3 day.
2. For loading rates up to 5.63 kg COD/m^3 day, long-term stable removal efficiencies over 99% were attained for backwashing strategy.
3. For loading rates up to 3.52 kg COD/m^3 day, long-term stable removal efficiency was attained for the two non-use strategies without backwashing. Thus for these loading rates, the two non-use strategies can be used as another means of biomass control.
4. For a 7.04 kg COD/m^3 day loading rate, backwashing and non-use strategies could not achieve consistent 99% removal efficiencies; neither did the combined operation of backwashing and non-use periods.

5. The pseudo-first-order removal rate constant decreased with an increase in MEK loading rate for all the three strategies. The non-use strategies showed superior removal rate than the backwashing strategy for loading rates below 3.52 kg COD/m^3 day.

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References

[1] G.A. Sorial, F.L. Smith, M.T. Suidan, P.J. Smith, P. Biswas, R.C. Brenner, Evaluation of performance of trickle bed biofilter—impact of periodic removal of accumulated biomass, in: Presented at 87th Annual Meeting and Exhibition of the Air and Waste Management Association, Paper No. 94-RA115A.05, Cincinnati, OH, 1994.

[2] G.A. Sorial, F.L. Smith, M.T. Suidan, P. Biswas, R.C. Brenner, Evaluation of trickle-bed biofilter media for toluene removal, J. Air Waste Manage. Assoc. 45 (1995) 801–810.

[3] J. Liira, V. Riihimaki, P. Pfaffli, Kinetics of methyl ethyl ketone in man: absorption, distribution and elimination in inhalation exposure, Int. Arch. Occup. Environ. Health 60 (1988) 195–200.

[4] H. Altenkirch, G. Stoltenburg, H.M. Wagner, Experimental studies on hydrocarbon neuropathies induced by methyl ethyl ketone, J. Neurol. 219 (1978) 159–170.

[5] W.H. Ralston, R.L. Hilderbrand, D.E. Uddin, M.E. Andersen, R.W. Gardier, Potentiation of 2,5-hexanedione neurotoxicity by methyl ethyl ketone, Toxicol. Appl. Pharmacol. 81 (1985) 319–327.

[6] M.A. Deshusses, G. Hamer, I.J. Dunn, Behavior of biofilters for waste air biotreatment. 1. Dynamic-model development, Environ. Sci. Technol. 29 (1995) 1048–1058.

[7] M.A. Deshusses, G. Hamer, I.J. Dunn, Behavior of biofilters for waste air biotreatment. 2. Experimental evaluation of a dynamic-model, Environ. Sci. Technol. 29 (1995) 1059–1068.

[8] M.A. Deshusses, G. Hamer, I.J. Dunn, Transient-state behavior of a biofilter removing mixtures of vapors of MEK and MIBK from air, Biotechnol. Bioeng. 49 (1996) 587–598.

[9] M.A. Deshusses, C.T. Johnson, Development and validation of a simple protocol to rapidly determine the performance of biofilters for VOC treatment, Environ. Sci. Technol. 34 (2000) 461–467.

[10] M.S. Chou, J.J. Huang, Treatment of methylethylketone in air stream by biotrickling filters, J. Environ. Eng. 6 (1997) 569–576.

[11] W.M. Moe, C. Li, Comparison of continuous and sequencing batch operated biofilters for treatment of gas-phase methyl ethyl ketone, J. Environ. Eng. 130 (2004) 300–313.

[12] J.C. Atoche, W.M. Moe, Treatment of MEK and toluene mixtures in biofilter: effect of operating strategy on performance during transient loading, Biotechnol. Bioeng. 86 (2004) 468–481.

[13] W.M. Moe, B. Qi, Performance of a fungal biofilter gas-phase solvent mixtures during intermittent loading, Water Res. 38 (2004) 2259–2268.

[14] F.L. Smith, G.A. Sorial, M.T. Suidan, A.W. Breen, P. Biswas, R.C. Brenner, Development of two biomass control strategies for extended, stable operation of highly efficient biofilters with high toluene loadings, Environ. Sci. Technol. 30 (1996) 1744–1751.

[15] F.L. Smith, G.A. Sorial, M.T. Suidan, P. Biswas, R.C. Brenner, Pilot-scale evaluation of alternative biofilter attachment media for the treatment of VOCs, in: Proceedings of the EPA Symposium on Bioremediation of Hazardous Wastes: Research, Development, and Field Evaluations, 1996, pp. 89–97.

[16] Standard Methods for the Examination of Water and Wastewater, 20th ed., APHA, AWWA, and WEF, 1998.